Fate of Irgarol 1051, diuron and their main metabolites in two UK marine systems after restrictions in antifouling paints

Article (Unspecified)

Fate of Irgarol 1051, diuron and their main metabolites in two UK marine systems after restrictions in antifouling paints

Georgia Gatidou[a,b], Nikolaos S. Thomaidis[c], John L. Zhou[a*]

[a]*Department of Biology and Environmental Science, School of Life Sciences, University of Sussex, Falmer, Brighton, BN1 9QJ, UK*

[b]*Water and Air Quality Laboratory, Department of Environmental Studies, University of the Aegean, University Hill, 81100 Mytilene, Greece*

[c]*Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimioupolis Zografou, 15771 Athens, Greece*

*Corresponding author:
Department of Biology and Environmental Science
School of Life Sciences
University of Sussex
Falmer
Brighton, BN1 9QJ
UK
Tel: 44 1273 877318
Fax: 44 1273 677196
Email: j.zhou@sussex.ac.uk

Abstract

Two major antifouling biocides used worldwide, Irgarol 1051 and diuron, and their degradation products in Shoreham Harbour and Brighton Marina, UK were studied during 2003-2004. The highest concentrations of Irgarol 1051 were 136 and 102 ng L^{-1} in water and 40 and 49 ng g^{-1} dry weight in sediments for Shoreham Harbour and Brighton Marina, respectively. As the degradation product of Irgarol 1051, M1 was also widespread, with the highest concentration of 59 ng L^{-1} in water and 23 ng g^{-1} in sediments in Shoreham Harbour, and 37 ng L^{-1} in water and 5.6 ng g^{-1} in sediments in Brighton Marina. The target compounds showed enhanced concentrations during the boating season (May – July), when boats were being re-painted (January – February), and where the density of pleasure crafts was high. Overall, the concentration of Irgarol 1051 decreased significantly from late 2000 to early 2004, indicating the effectiveness of controlling its concentrations in the marine environment following restricted use. Diuron was only detected in 14% of water samples, and mostly absent from sediment samples.

Keywords: Antifouling paints; Irgarol 1051; Diuron; Metabolites; Seawater, Marine sediment

1. Introduction

The serious environmental problems caused by the extensive use of tributyltin in antifouling paints, e.g. imposex in dogwhelks, resulted in the introduction of alternative compounds for the protection of ship hulls. Irgarol 1051 (2-methylthio-4-*tert*-butylamino-6-cyclopropylamino-s-triazine) and diuron (1-(3,4 dichlorophenyl)-3,3 dimethyl urea) are two of such substances, which have been used worldwide as active ingredients for this purpose. Prior to September 2000, eight organic compounds including Irgarol 1051 and diuron were allowed for use in antifouling paints in the UK. After September 2000, as a result of 98/8/EE directive implementation, restrictions concerning the use of such substances in antifoulants were instituted. According to these restrictions, antifouling paints for use in small vessels are allowed to contain only the substances dichlofluanid, zineb and zinc pyrithione. Irgarol 1051 was approved for use on larger (> 25 m) vessels up to July 2003 (Bowman et al., 2003), whereas diuron is no longer approved for use as an active ingredient in antifouling paints on vessels of any size.

It is well known that the more stable in the environment a compound is the more effective the antifouling paint becomes because the protection of the vessels lasts longer. For this reason stable compounds are preferred in paint industries. As a result, even after a booster biocide is banned it may still be detected in the marine environment. Furthermore, degradation products of these compounds may also be detected as a result of natural transformation processes such as photodegradation and biodegradation (Lam et al., 2005).

Although Irgarol 1051 is not considered to be easily degraded in seawater with a half-life of approximately 100 days, recent studies (Liu et al., 1999) show that it can be degraded to form its main metabolite M1 (2-methylthio-4-*tert*-butylamino-s-triazine) through *N*-dealkylation. Concentrations of Irgarol 1051 in seawater worldwide vary between non-detectable and low parts per billion. Concentrations up to 4.2 μg L^{-1} have been detected in coastal areas (Basheer et al., 2002), whereas in the UK the highest concentration observed is

1.4 μg L^{-1} (Thomas et al., 2001). In sediment samples concentrations as high as 1 μg g^{-1} have been detected in marinas (Boxall et al., 2000). The levels of M1 are up to 1.9 μg L^{-1} (Okamura et al., 2000) and 0.003 μg g^{-1} (Ferrer and Barceló, 2001) for seawater and marine sediment respectively, which are generally lower than those of Irgarol 1051 indicating slow degradation rates of the parent compound.

Although considered to be relatively persistent in seawater, diuron may be degraded by *N*-dimethylation under aerobic conditions to metabolites including DCPMU (1-(3,4 dichlorophenyl)-3 methyl urea), DCPU (1-(3,4 dichlorophenyl) urea) and DCA (3,4 dichloroaniline). Diuron concentrations up to 6.7 μg L^{-1} (Thomas et al., 2001) and 1.4 μg g^{-1} (Thomas et al., 2000) have been detected in seawater and marine sediment samples, whereas among its degradation products only DCPMU and DCPU have been detected in seawater at concentrations ranging between 0.001 and 0.078 μg L^{-1} and between 0.001 and 0.006 μg L^{-1} respectively (Thomas et al., 2002). DCPMU has also been detected in sediments at concentrations below 0.025 μg g^{-1} (Martinez and Barceló, 2001).

The aim of this study was to investigate the levels of Irgarol 1051, diuron and their main degradation products (M1, DCPMU, DCPU and DCA) in Shoreham Harbour and Brighton Marina, UK, following the restrictions of their use in antifouling paints. Spatial and temporal variations of these compounds in seawater and sediment were investigated. Furthermore, the relationship between the physicochemical properties of seawater and marine sediment and the concentrations of the target compounds was also examined in order to identify geochemical controls.

2. Materials and methods

2.1. Chemicals

Analytical standards of Irgarol 1051, diuron and its degradation products were supplied by Dr. Ehrenstorfer (Germany). M1 was a gift of both the Centre for Environment, Fisheries and

Aquaculture Science (Essex, UK) and Ciba-Geigy (NY, USA). Atrazine-d_5 from QMX Laboratories (UK) was used as the internal standard. Ultrapure and HPLC-grade water was prepared in the laboratory with a Maxima HPLC/LS system supplied by ELGA (UK) and a MilliQ/MilliRO Millipore system (USA). Stock solutions in methanol were prepared at 1000 mg L^{-1} for Irgarol 1051, diuron and their degradation products, and at 500 mg L^{-1} for atrazine-d_5. The organic solvents acetonitrile, dichloromethane, methanol, ethyl acetate and acetone were of glass-distilled grade (Rathburns, Scotland). HPLC grade acetonitrile and methanol were purchased from Merck (Germany).

2.2. Description of study areas

Shoreham Harbour (Fig. 1a) is situated on the South Coast of England in West Sussex and located 5 miles to the West of the city of Brighton & Hove. Inside the harbour and above the main channel is situated the Lady Bee Marina with berths for 120 vessels. Another small marina called Emerald Quay is situated on the West of the harbour. Brighton Marina (Fig. 1b) is situated half a mile from the centre of Brighton. It is the largest marina in the UK, at over 126 acres with berths for 1300 vessels. The marina is subject to winds causing sand banks to form, thus it requires annual dredging (Bowman et al., 2003).

2.3. Sample collection

Sub-surface (0.5 m) seawater samples were collected in pre-cleaned amber glass bottles (2.5 L). The bottles were placed in a stainless steel frame fitted with a spring-loaded PTFE stopper that was opened and closed underneath water so as to minimise surface microlayer. The samples were then filtered through 0.7-μm GF/F filter papers (Whatman), spiked with 100 ng of atrzine-d_5, and stored at 4^{o}C till further processing. Measurements of salinity, conductivity and pH were taken in situ using a WTW Multiline P4 Universal Meter with a Tetra Con 325 salinity probe and a SenTix 41-3 pH electrode. Surface sediment samples were collected

using a hand held Van Veen sediment grab. The sediment samples were transferred to pre-cleaned glass sediment jars and stored at -18^{o}C till analysis.

Sample collection was performed from March 2003 to February 2004. Three sampling campaigns took place in Brighton Marina (03/2003, 12/2003 and 02/2004) where samples were collected from 15 sites throughout the marina, whereas in Shoreham Harbour 9 sampling trips were undertaken (03/2003, 05/2003, 07/2003, 08/2003, 10/2003, 11/2003, 12/2003, 01/2004, 02/2004) where samples were taken from 9 sites.

2.4. Characterisation of marine sediments

In order to measure the pH of marine sediments, each sample (4 g dry weight) was placed in a test tube to which 5 mL of pure water was added. The test tubes were closed and agitated vigorously for 5 min. Then, another 5 mL of pure water was added to the test tube and the samples mechanically agitated for 15 min. The samples were left for 10 min before the pH of the supernatant was measured using the WTW Multiline P4 Universal meter.

The particle size distribution of the sediment samples was accomplished by sieving. Samples (10 g dry weight) were sequentially passed through two sieves with pore size of 180 and 63 μm so as to obtain three size fractions: >180 μm, 180 – 63 μm and <63 μm respectively.

For the determination of organic carbon content appropriate tin boats (8 x 5 mm) were cleaned with chloroform, acetone and finally pure water. Sediment samples (10 mg) in triplicate were accurately weighed into the boats, and acidified with sulphuric acid for 24 h so as to remove carbonate. Then the tin boats were closed and placed into the autosampler of a Carlo Erba elemental analyser for the analysis. For the calibration of the instrument an external standard of acetanilide (Thermoquest, Italy) was used. Results were validated by the use of a Certified Reference Material (Mess-2) from the National Research Council of Canada, which is a marine sediment containing 2.14±0.03% organic carbon.

2.5. Sample extraction and analysis

Isolation of the target compounds from seawater samples was performed using a solid-phase extraction (SPE) procedure, following a method developed by Gatidou et al. (2005). Briefly, SPE cartridges (Isolute ENV$^+$, 1 g) were activated with 10 mL each of methanol and ultrapure water. The extraction was performed at a flow rate of 10 mL min^{-1}. Following extraction, the cartridges were washed with 4 × 2.5 mL of ultrapure water, dried for 3 min and eluted with 3 × 2 mL of methanol. The eluents were evaporated to dryness under a gentle stream of nitrogen (35°C) and re-dissolved in 300 μL of ethyl acetate.

In order to increase the preconcentration factor, a volume of 2 L was extracted for the determination of Irgarol 1051 and M1 using SPE cartridges with a high sorbent mass (1 g). The recoveries of the two compounds at three levels (10, 100, 1000 ng L^{-1}) ranged between 82.0 and 96.4% for M1 and from 94.6 to 116% for Irgarol 1051. The method remained repeatable (n=6) and reproducible (k=3, n=20) with RSD ≤ 2.5%. The limits of detection (LODs) were found to be 0.5 and 3.1 ng L^{-1} for M1 and Irgarol 1051, respectively.

Sediment samples for the determination of Irgarol 1051 and M1 were extracted using microwave-assisted extraction as described previously (Gatidou et al., 2004b). Briefly, 3 g of marine sediment spiked with 100 ng of internal standard were extracted with 30 mL of water at 115°C for 10 min using a MARS-X microwave accelerated extraction system. The LODs of the two compounds were 0.9 and 1.7 ng g^{-1} (dry weight) for M1 and Irgarol 1051.

Isolation of diuron and its main degradation products from marine sediment samples was performed by extracting dry sediment (2 g) twice with 20 mL of methanol by sonication for 30 min at 50°C, following an established method (Gatidou et al., 2004a). The LODs of the compounds ranged between 1.7 (DCPU) and 4.0 (DCPMU) ng g^{-1} (dry weight). Sample extracts were analysed for Irgarol 1051 and M1 using gas chromatograph-mass spectrometry (GC-MS) as described previously (Gatidou et al., 2004b), and for ureas and DCA using high

performance liquid chromatography-diode array detection (HPLC-DAD) as described by Gatidou et al. (2004a).

3. Results and discussion

3.1. Concentrations of Irgarol 1051 and M1 in seawater

Concentrations of Irgarol 1051 in seawater samples ranged from <3.1 to 136 ng L^{-1} and from <3.1 to 102 ng L^{-1} for Shoreham Harbour and Brighton Marina respectively, which are in accordance with those detected in similar environments in the UK and worldwide (Table 1). Hughes and Alexander (1993) suggests that when the concentration of Irgarol 1051 exceeds 136 ng L^{-1} (EC_{50}) serious damage may be caused to some phytoplanktonic microorganisms such as the diatom *Navicula pelliculosa*. Furthermore, Dahl and Blanck (1996), working with a periphyton community in a flow through microcosm, found that at concentrations as low as 63 ng L^{-1}, Irgarol 1051 significantly decreased photosynthetic activity.

The observed mean concentration (18.3 ng L^{-1}) in Shoreham Harbour was slightly higher than that in Brighton Marina (14.1 ng L^{-1}), probably due to the fact that the use of Irgarol 1051 in small vessels (< 25 m), likely to be dominating in the marina, is prohibited in the UK (Thomas et al., 2002). Furthermore, the daily entrance of large commercial vessels in the harbour, for which there are no restrictions concerning the usage of Irgarol 1051, might be responsible for the higher concentrations of the compound in this area.

The highest concentrations of Irgarol 1051 in Shoreham Harbour were detected in May and July 2003 (Fig. 2a), probably because of the higher boating activity during these months (Biselli et al., 2000; Lamoree et al., 2002). During autumn and winter months the concentrations of Irgarol 1051 were lower in most samples. High concentrations of Irgarol 1051 in the harbour during March 2003 and from January to February 2004 probably resulted from the scrubbing and re-application of antifouling paints so that the vessels were ready for the new boating season (Bowman et al., 2003). Since higher leaching rates are expected soon

after the application of the paint on the hulls (Hall et al., 1999) this distribution of concentration is expected. In Brighton Marina the highest concentrations of Irgarol 1051 were also detected in July 2003 (Fig. 2b), and generally there was a clear temporal variation in Irgarol 1051 concentration which decreased from July 2003 to February 2004.

Bowman et al. (2003) also studied the presence of Irgarol 1051 in Brighton Marina. The comparison of the results between the two studies shows that the concentration of this compound reached a peak in late 2000, after which it started to decline (Fig. 3). The findings confirm the effectiveness of the restrictions concerning the use of this compound.

The concentrations of M1 ranged from <0.5 to 58.9 ng L^{-1} for Shoreham Harbour and from <0.5 to 36.9 ng L^{-1} for Brighton Marina, which are consistent with other studies (Table 2). This is the first time that this compound was detected in Brighton Marina and Shoreham Harbour. The mean concentrations of M1 were always lower than those of the parent compound (Fig. 2) suggesting slow degradation rate of Irgarol 1051 as mentioned before. However, in some sites the concentration of M1 was either higher than that of Irgarol 1051, such as in the station Surry Boat Yard in July 2003 where the observed concentrations were 58.9 and 32.4 ng L^{-1} for M1 and Irgarol 1051 respectively, or only the metabolite was detected (station Middle Pier in February 2004). The results show similar temporal distribution of M1 to Irgarol 1051 in Shoreham Harbour with the highest concentrations from May to July 2003, although there was no clear trend concerning its spatial distribution.

3.2. Concentrations of diuron and its main metabolites in seawater

Diuron was detected in Shoreham Harbour during the high boating season, from May to October 2003, with concentrations between < 7 and 366 ng L^{-1}, whereas in Brighton Marina it was detected in a few samples in July 2003 at concentrations between 69.7 and 236 ng L^{-1}. Although the levels found in this study are consistent with other studies (Dahl and Blanck, 1996; Boxall et al., 2000; Okamura et al., 2003), the presence of diuron was unexpected

considering the restrictions on its use in the UK. As a result, the likely explanation for its detection was the entrance both in the harbour and marina of vessels from countries where diuron is still in use. The detected concentrations of diuron are low compared with its estimated EC_{50} value for several photosynthetic organisms (Fernandez-Alba et al., 2002). Since the compound was only detected in a small number of samples (14%) it was difficult to reach a conclusion about its temporal and spatial trends. None of the three main metabolites of diuron (DCPMU, DCPU, DCA) was detected in any seawater samples.

3.3. Concentrations of Irgarol 1051 and M1 in marine sediments

Irgarol 1051 was detected in sediment samples at concentrations between <1.7 and 40 ng g^{-1} and from <1.7 and 49.3 ng g^{-1} in Shoreham Harbour and Brighton Marina respectively (Tables 1 and 2). The mean concentration of the compounds was higher in the harbour than in the marina. The observed concentrations are of the same order of magnitude as those reported by others (Biselli et al., 2000; Albanis et al., 2002; Bowman et al., 2003).

During the first sampling in Brighton Marina dredging of the marina was taking place. As shown in Fig. 2b, the levels of Irgarol 1051 in seawater samples gradually decreased after dredging, whereas in sediment its concentration was slightly decreased during the second sampling and then increased during the third one (Fig. 4). The results therefore do not support a conclusion that dredging may induce desorption of previously adsorbed compounds from sediments, which will depend on factors such as the type of dredger and the kinetics of chemical desorption from sediments. In addition, the concentrations of Irgarol 1051 found in the present study are low compared with those detected in the same area three years earlier as reported by Bowman et al. (2003).

Concentrations of M1 in Shoreham Harbour ranged between <0.9 and 22.7 ng g^{-1}, whereas in Brighton Marina between <0.9 and 5.6 ng g^{-1} which are in accordance with other studies

(Thomas et al., 2000; Martinez and Barceló, 2001; Okamura et al., 2003). Mean concentrations of M1 were in all cases lower than those of the parent compound.

3.4. Concentrations of diuron and its main metabolites in marine sediments

From all the samples analysed, diuron was detected only in two samples taken from Shoreham Harbour and specifically in Lady Bee marina (66.4 ng g^{-1}) and Old Fort (59.7 ng g^{-1}) in November 2003 and January 2004 respectively. Similar concentrations of the compound have been reported by others (Boxall et al., 2000; Martinez and Barceló, 2001).

The general absence of diuron from sediment samples was expected since it is a hydrophilic compound and thus its adsorption onto sediment is very limited (Thomas et al., 2000). The detection of the compound in the two samples referred above was probably due to its release from adsorbed paint particles and subsequent re-adsorption onto sediment (Thomas et al., 2000).

DCPMU was the only metabolite of diuron, which was detected during the present study. Its concentrations ranged between <4 and 122 ng g^{-1} in Shoreham Harbour and between <4 to 56.5 ng g^{-1} in Brighton Marina. Martinez and Barceló (2001) have also detected DCPMU in marine sediment samples in concentrations < 25 ng g^{-1}.

3.5. Statistical analyses

The effects of salinity and pH on contaminant concentrations were examined for Irgarol 1051 and M1 since these were the only compounds which were detected in most of the samples. Statistical analysis of the results was accomplished (Statistica 5.5, 1984-1999, StatSoft Inc.) to examine if there was a correlation between the physicochemical properties of water and the detected concentrations of the compounds. Spearman non-parametric correlation was applied and the results for the two sampling areas are given in Table 3.

Statistical analysis confirmed the expected correlation between the concentrations of the parent compound Irgarol and its metabolite M1. No correlation was observed between the observed concentrations and salinity for both sampling areas. The results are in accordance with Sargent et al. (2000) and Bowman et al. (2003) but in contrast with Steen et al. (1997) who observed a linear relationship between salinity and the concentration of Irgarol 1051. It is difficult to assess the correlation between pH and M1 concentrations since there was a small variation of water pH values (5.5 – 8.0). Previously, no correlation was found between pH and the concentrations of Irgarol 1051 (Sargent et al., 2000; Bowman et al., 2003). The statistical analyses for sediment samples are shown in Table 4. Since the fine fraction of the sediment is usually related with a high percentage of organic carbon content, existence of a correlation was only examined between particles <63 μm and the concentrations of the compounds. The results reiterated the correlation between the concentrations of Irgarol 1051 and M1.

According to the results a correlation was observed both between pH and organic carbon content and the concentrations of the two compounds in Shoreham Harbour, whereas the fine fraction seemed to be correlated only with the concentrations of Irgarol 1051. In Brighton Marina correlation was observed between the concentrations of M1 and pH and the fine fraction of marine sediment. The observed correlation between the organic carbon content and the fine fraction of the sediment samples was expected.

The different correlations between physicochemical properties of the sediment samples and the concentrations of the two compounds probably are due to the different age and composition of the sediment in the two sampling areas. It is well known that properties such as pH, particle size, and the amount and nature of organic matter play an important role during the complex adsorption process. The Shoreham Harbour and Brighton Marina receive inputs from different rivers, hence may have different organic matter in their sediments. Annual dredging of sediments can cause further complications to sediment composition, hence its capacity to adsorb contaminants.

3.6. Sediment/water partitioning

Since the partitioning of a compound between the aquatic compartments is of high importance in defining its bioavailability, the distribution coefficient (K_d, mL g^{-1}) was calculated for Irgarol 1051 and M1:

$$K_d = \frac{C_s}{C_w} \; 1000 \qquad (1)$$

where C_s is the concentration of the compound in sediment (ng g^{-1}), and C_w is the concentration of the compound in water (ng L^{-1}).

As the partition of organic contaminants between sediment and water is controlled by the organic matter of sediments, the organic carbon normalized partition coefficient (K_{oc}) was estimated using the following equation:

$$K_{oc} = \frac{K_d}{\% \text{ Organic carbon}} \qquad (2)$$

As shown in Table 5, K_d values ranged between 18 and 4902 and between 103 and 7833 mL g^{-1} for Irgarol 1051 and M1 respectively, which are equivalent to 2 to 5 and 1 to 5 in log(K_{oc}) for the two compounds. Such log(K_{oc}) values for Irgarol 1051 are comparable with the theoretical log(K_{oc}) values calculated by Thomas et al. (2002) and the values determined by Comber et al. (2002) under laboratory conditions for different suspended solid concentrations. The log(K_{oc}) values determined for Irgarol 1051 in Brighton Marina by Bowman et al. (2003) are slightly higher than those found in the present work probably due to reduction of its environmental concentrations as a result of the restrictions concerning its use.

4. Conclusions

Regular sampling in Shoreham Harbour and Brighton Marina has shown the presence of Irgarol 1051, diuron and their metabolites both in seawater and marine sediments even after their restricted use in the UK. The highest mean concentrations were observed during the high boating season and the period when the vessels were re-painted. In Shoreham Harbour the

highest concentrations were detected in those samples collected from the two marinas situated inside the harbour (Lady Bee Marina and Emerald Quay), reiterating the fact that the presence of antifouling booster biocides is related to their use in antifouling paints. The observed concentrations are comparable to those observed in other European coastal waters. Overall, the concentration of Irgarol 1051 has declined substantially following its restricted use, confirming the effectiveness of such measures.

Statistical analysis of the results showed no correlation between salinity and the concentrations of Irgarol 1051 and M1. Water pH values were correlated only with the concentrations of M1 in Brighton Marina. For sediment samples there was a strong correlation between sediment physicochemical properties and the concentrations of Irgarol 1051 and M1 in Shoreham Harbour. In Brighton Marina correlation was observed only between pH and concentrations of M1.

Acknowledgements

This work was funded by a Marie Curie Host Fellowship from the EU 5th Framework Program (Contract No. HPMT-CT-2000-00181) and a Leverhulme Trust Research Grant to J. Zhou (Grant No. F/00230/H). The authors would like to thank K. Thomas (CEFAS) and R. Balcomb (Ciba-Geigy) for the offer of M1, and T. Frickers and J. Readman (Plymouth Marine Laboratory) for sediment organic carbon analysis.

References

Albanis TA, Lambropoulou DA, Sakkas VA, Konstantinou IK. Antifouling paint booster biocide contamination in Greek marine sediments. Chemosphere 2002;48:475–485.

Basheer C, Tan KS, Lee HK. Organotin and Irgarol 1051 contamination in Singapore coastal waters. Marine Pollution Bulletin 2002;44:697–703.

Biselli S, Bester K, Huhnerfuss H, Fent K. Concentrations of the antifouling compound Irgarol 1051 and of organotins in water and sediments of German North and Baltic Sea marinas. Marine Pollution Bulletin 2000;40:233–243.

Bowman JC, Readman JW, Zhou JL. Seasonal variability in the concentrations of Irgarol 1051 in Brighton Marina, UK; including the impact of dredging. Marine Pollution Bulletin 2003;46:444–451.

Boxall ABA, Comber SD, Conrad AU, Howcroft J, Zaman N. Inputs, monitoring and fate modelling of antifouling biocides in UK Estuaries. Marine Pollution Bulletin 2000;40:898–905.

Comber SDW, Franklin G, Gardner MJ, Watts CD, Boxall ABA, Howcroft J. Partitioning of marine antifoulants in the marine environment. The Science of the Total Environment 2002;286:61–71.

Dahl B, Blanck H. Toxic effects of the antifouling agent Irgarol 1051 on periphyton communities in coastal water microcosms. Marine Pollution Bulletin 1996;32:342–350.

Fernandez-Alba AR, Hernando MD, Piedra L, Chisti Y. Toxicity evaluation of single and mixed antifouling biocides measured with acute toxicity bioassays. Analytica Chimica Acta 2002;456:303-312.

Ferrer I, Barceló D. Identification of a new degradation product of the antifouling agent Irgarol 1051 in natural samples. Journal of Chromatography A 2001;926:221–228.

Gardinali PR, Plasencia MD, Maxey C. Occurrence and transport of Irgarol 1051 and its major metabolite in coastal waters from South Florida. Marine Pollution Bulletin 2004;49:1072-1083.

Gatidou G, Kotrikla A, Thomaidis NS, Lekkas TD. Determination of two antifouling booster biocides and their degradation products in marine sediments by high performance liquid chromatography-diode array detection. Analytica Chimica Acta 2004a;505:153-159.

Gatidou G, Kotrikla A, Thomaidis NS, Lekkas TD. Determination of the antifouling booster biocides Irgarol 1051 and diuron and their metabolites in seawater by high performance liquid chromatography - diode-array detector. Analytica Chimica Acta 2005;528:89-99.

Gatidou G, Zhou JL, Thomaidis NS. Microwave-assisted extraction of Irgarol 1051 and its main degradation product from marine sediments using water as the extractant followed by gas chromatography–mass spectrometry determination. Journal of Chromatography A 2004b;1046:41-48.

Gough MA, Fothergill J, Hendrie JD. A survey of southern England coastal waters for the s-triazine antifouling compound Irgarol 1051. Marine Pollution Bulletin 1994;28:613–620.

Hall LW, Giddings JM, Solomon KR, Balcomb R. An ecological risk assessment for the use of Irgarol 1051 as an algaecide for antifoulant paints. Critical Reviews in Toxicology 1999;29:367–437.

Hughes J, Alexander MM. The toxicity of irgarol 1051 to *Selenastrum capricornutum* (study ID B267-582-1), *Anabaena flos-aquae* (study ID B267-582-2), *Navicula pelliculosa* (study ID B267-582), *Skeletonema costatum* (study ID B267-582-4), Malcolm Pirnie Inc., Terrytown, NY, 1993.

Lam KH, Cai, Z, Wai H-Y, Tsang VW-H, Lam MH-W, Cheung RY-H, Yu H, Lam PK-S. Identification of a new Irgarol 1051 related s-triazine species in coastal waters. Environmental Pollution 2005;136:221-230.

Lamoree MH, Swart SP, Van der Horst A, Van Hattum B. Determination of diuron and the antifouling paint biocide Irgarol 1051 in Dutch marinas and coastal waters. Journal of Chromatography A 2002;970:183–190.

Liu D, Pacepavicious GJ, Maguire RJ, Lau YL, Okamura H, Aoyama I. Mercuric chloride-catalyzed hydrolysis of the new antifouling compound Irgarol 1051. Water Research 1999;33:155–163.

Martinez K, Barceló D. Determination of antifouling pesticides and their degradation products in marine sediments by means of ultrasonic extraction and HPLC-APCI-MS. Fresenius' Journal of Analytical Chemistry 2001;370:940-945.

Okamura H, Aoyama I, Liu D, Maguire RJ, Pacepavicius GJ, Lau YL. Fate and ecotoxicity of the new antifouling compound Irgarol 1051 in the aquatic environment. Water Research 2000;34:3523 –3530.

Okamura H, Aoyama I, Ono Y, Nishida T. Antifouling herbicides in the coastal waters of western Japan. Marine Pollution Bulletin 2003;47:59–67.

Readman JW, Wee Knong LL, Grondin D, Barocci J, Vileneuve LP, Mee LD. Coastal water contamination from a triazine herbicide used in antifouling paints. Environmental Science and Technology 1993;27:1940–1942.

Sakkas VA, Konstantinou, IK, Lambropoulou DA, Albanis TA. Survey for the occurrence of antifouling paint booster biocides in the aquatic environment of Greece. Environmental Science and Pollution Research 2002;9:327–332.

Sargent CJ, Bowman JC, Zhou JL. Levels of antifoulant irgarol 1051 in the Conwy Marina, North Wales. Chemosphere 2000;41:1755–1760.

Steen RJCA, Leonards PEG, Brinkman Th, Cofino WP. Ultra-trace-level determination of the antifouling agent Irgarol 1051 by gas chromatography with tandem mass spectrometric detection. Journal of Chromatography A 1997;766:153–158.

Thomas KV, Blake SJ, Waldock .MJ. Antifouling paint booster biocide contamination in UK marine sediments. Marine Pollution Bulletin 2000;40:739-745.

Thomas KV, Fileman TW, Readman JW, Waldock M. Antifouling paint booster biocides in the UK coastal environment and potential risks of biological effects. Marine Pollution Bulletin 2001;42:677–688.

Thomas KV, McHugh M, Waldock M. Antifouling paint booster biocides in UK coastal waters: inputs, occurrence and environmental fate. The Science of the Total Environment 2002;293:117-127.

Tolosa I, Readman JW, Blaevoet A, Ghilini S, Bartocci J, Horvat M. Contamination of Mediterranean (Cote d'Azur) coastal waters by organotins and Irgarol 1051 used in antifouling paints. Marine Pollution Bulletin 1996;32:335–341.

Zhou JL, Fileman TW, Evans S, Donkin P, Mantoura RFC, Rowland SJ. Seasonal distribution of dissolved pesticides and polynuclear aromatic hydrocarbons in the Humber estuary and Humber coastal zone. Marine Pollution Bulletin 1996;32:599–608.

Figure legends

Fig. 1. (a) Map of Shoreham Harbour showing the location of 9 sampling sites, and (b) map of Brighton Marina showing the location of 15 sampling sites.

Fig. 2. Temporal variation of the mean concentrations of M1, Irgarol 1051 and diuron in seawater samples taken from (a) Shoreham Harbour, and (b) Brighton Marina, UK.

Fig. 3. Changes in Irgarol 1051 concentrations with time: comparison of the results from this work with a previous study (Bowman et al., 2003).

Fig. 4. Temporal variation in the concentration of Irgarol 1051 in sediment samples from Brighton Marina and Shoreham Harbour, UK.

Fig. 1a

Fig. 1b

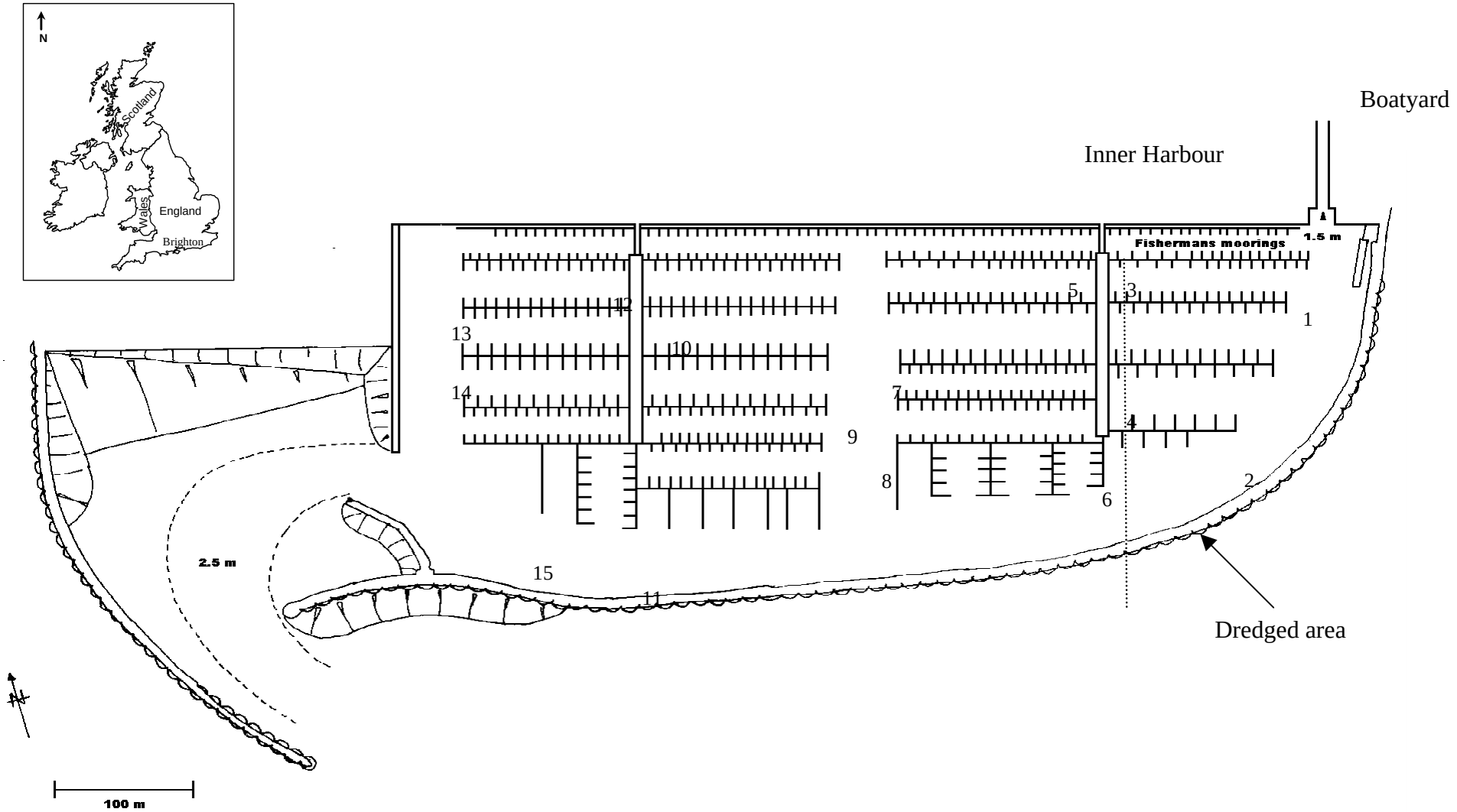
N
Scotland
Wales
England
Brighton
Boatyard
Inner Harbour
Fishermans moorings
1.5 m
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
2.5 m
Dredged area
100 m

Fig. 2

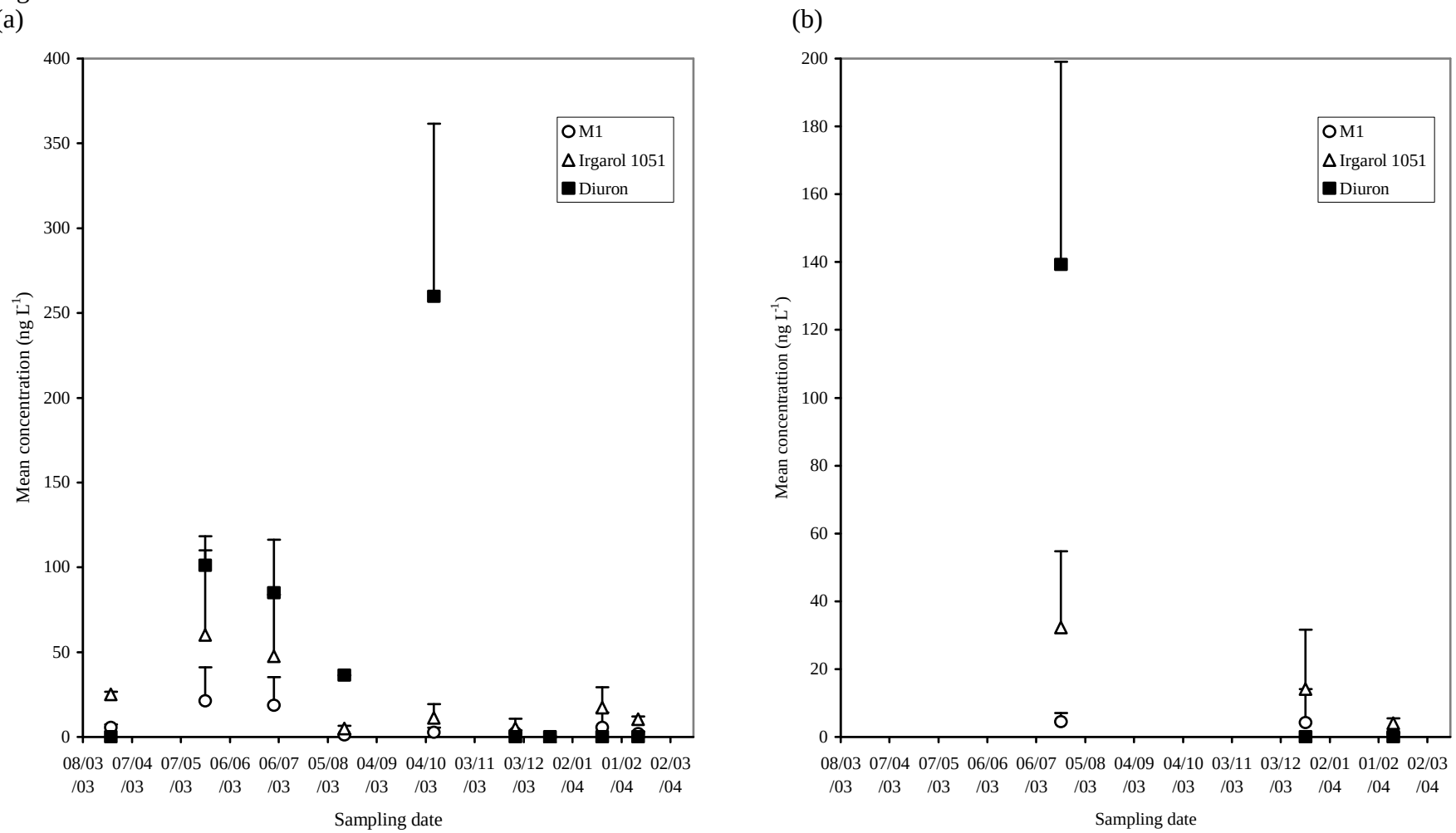
(a)
(b)
M1
Irgarol 1051
Diuron
Mean concentration (ng L-1)
Mean concentrattion (ng L-1)
Sampling date
08/03 /03
07/04 /03
07/05 /03
06/06 /03
06/07 /03
05/08 /03
04/09 /03
04/10 /03
03/11 /03
03/12 /03
02/01 /04
01/02 /04
02/03 /04

Fig. 3

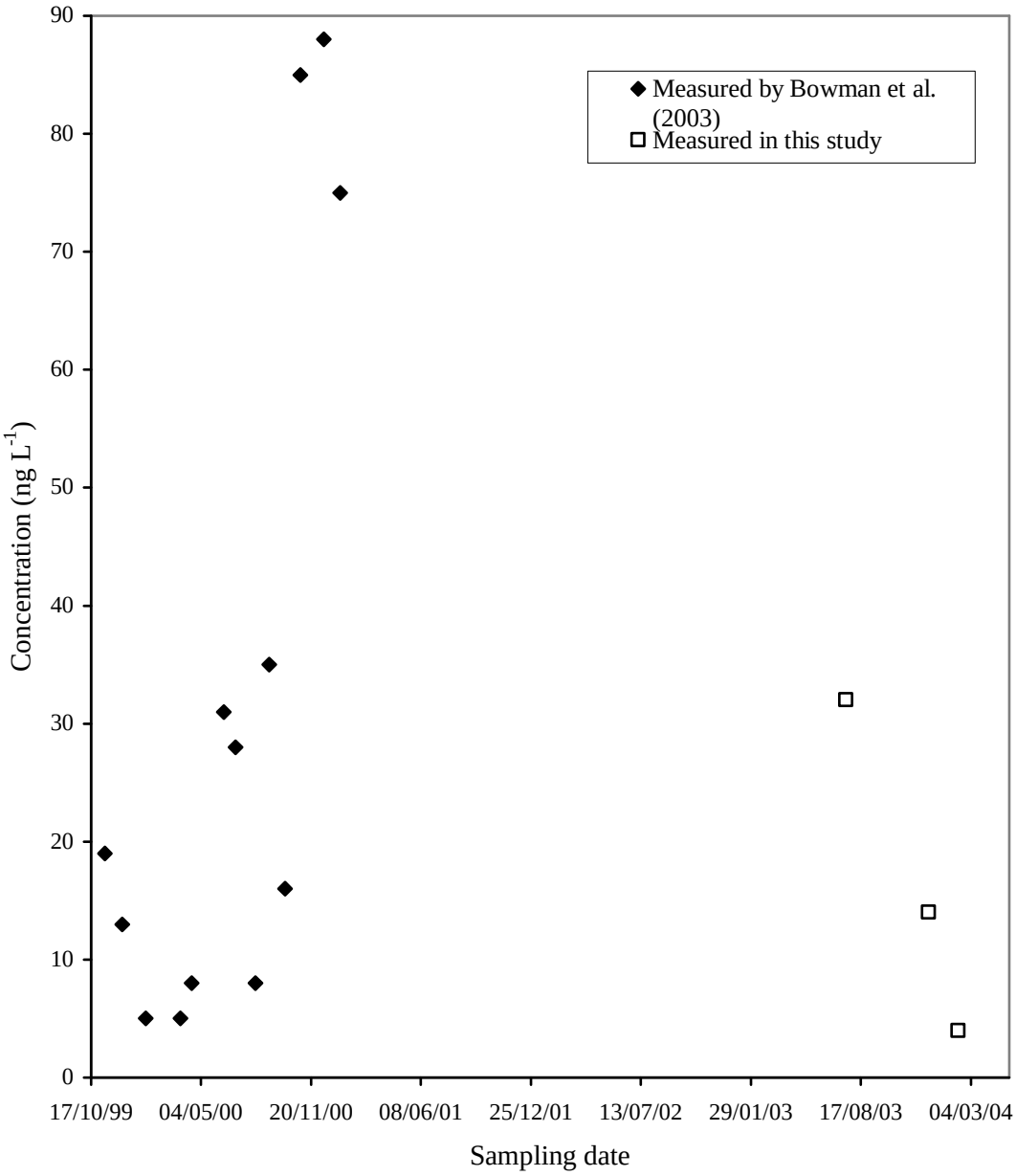
Measured by Bowman et al. (2003)
Measured in this study
Concentration (ng L-1)
Sampling date
0
10
20
30
40
50
60
70
80
90
17/10/99
04/05/00
20/11/00
08/06/01
25/12/01
13/07/02
29/01/03
17/08/03
04/03/04

Fig. 4

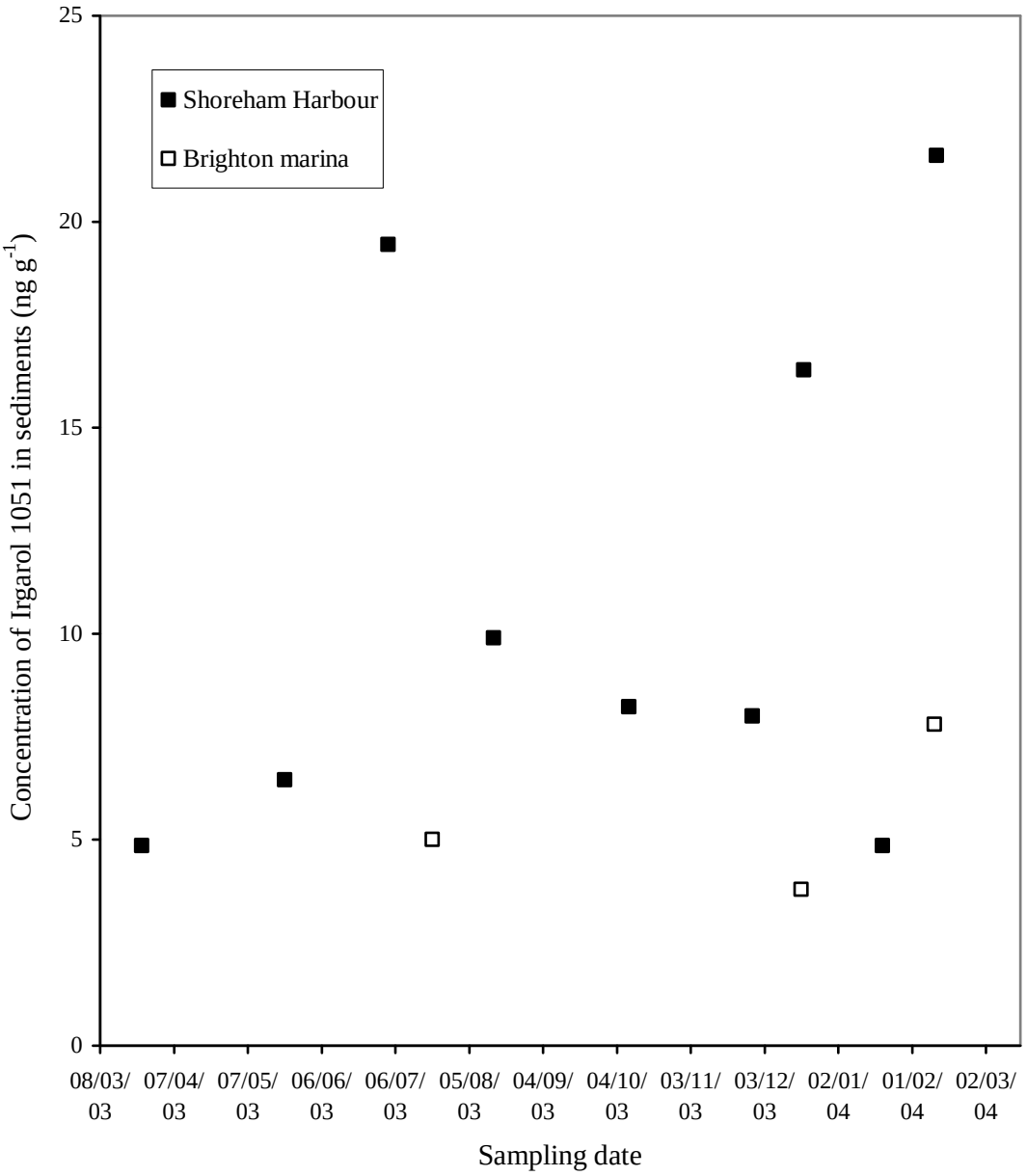
Shoreham Harbour
Brighton marina
Concentration of Irgarol 1051 in sediments (ng g-1)
25
20
15
10
5
0
08/03/03
07/04/03
07/05/03
06/06/03
06/07/03
05/08/03
04/09/03
04/10/03
03/11/03
03/12/03
02/01/04
01/02/04
02/03/04
Sampling date

Table 1.

Global comparison of the concentrations of Irgarol 1051 in seawater and marine sediments from different sites.

Sampling area	Sampling date	Seawater (ng L^{-1})	Sediment (ng g^{-1})	Reference
		Marinas		
Kent, Sussex, Hampshire	8/1993	52– 500	n.s.	Gough et al. (1994)
Sutton Harbour	4-10/1998	<1 – 69	n.s.	Thomas et al. (2001a)
Conwy, Wales	1-3/1999	7 – 543	n.s.	Sargent et al. (2000)
Southern coast	1-10/1999	<1-1421	n.s.	Thomas et al. (2001a)
Brighton	11/1999-1/2001	<1-964	<1-77	Bowman et al. (2003)
	3/2003-2/2004	<3.1-102	<1.7-49.3	This study
Humber	4-9/1995	169-682	n.s.	Zhou et al. (1996)
Côte d' Azur	6/1992	110-1700	n.s.	Readman et al. (1993)
Riviera, Monaco	5-6/1995	22-640	n.s.	Tolosa et al. (1996)
Greek marinas	10/1999-9/2000	≤68	37-350	Albanis et al. (2002)
North and Baltic sea	7-9/1997-1998	11-170	3-25	Biselli et al. (2000)
South Florida, USA	2000-2001	<1-182	n.s.	Gardinali et al. (2004)
Seto Inland Sea, Japan	8/1999	≤262	n.s.	Okamura et al. (2003)
		Ports		
Côte d' Azur	6/1992	<5-280	n.s.	Readman et al. (1993)
Riviera, Monaco	5-6/1995	13.8-264	n.s.	Tolosa et al. (1996)
Peraeus	10/1999-9/2000	10-24	≤19	Sakkas et al. (2002)
Thessaloniki	10/1999-9/2000	n.s.	≤11	Albanis et al. (2002)
Kalamata	5-6/2002	≤50	n.s.	Gatidou et al. (2005)
Patra	7/2002	120	n.s.	Gatidou et al. (2005)
Shoreham	3/2003-2/2004	<3.1-136	<1.7-40	This study

n.s. : not sampled

Table 2.

Summary of M1 concentrations in seawater and marine sediment samples from various locations.

Sampling area	Sampling date	Seawater (ng L^{-1})	Sediment (ng g^{-1})	Reference
Southampton Water	10/1998	13-99	<0.4-1.2	Thomas et al. (2000)
	summer 2000	<1-59	0-0.3	Thomas et al. (2002)
Catalonia	1-8/1999	<2-400	n.s.	Martinez et al. (2000)
Barcelona (Masnou)	2/1997-6/1998	≤23	0.2-3.3	Ferrer & Barceló (2001)
Mediteranean Coast		n.s.	<0.3-13	Martinez and Barceló (2001)
Seto Inland Sea	8/1999	≤80	n.s.	Okamura et al. (2003)
	7-8/1997	19.7-1270	n.d.	Okamura et al. (2000)
	5-11/1998	≤1870	n.d.	Okamura et al. (2000)
Brighton Marina	3/2003-2/2004	<0.5-36.9	<0.9-5.6	This study
Shoreham Harbour	3/2003-2/2004	<0.5-58.9	<0.9-22.7	This study

n.s.: not sampled, n.d.: not detected

Table 3.

Spearman non-parametric correlation between the concentrations of contaminants and the physicochemical properties of seawater samples from (a) Shoreham Harbour and (b) Brighton Marina, UK.

(a)

	M1	pH	Salinity
Irgarol 1051	**0.825**	-0.026	-0.099
M1		0.136	-0.210

pH	-0.462

(b)

	M1	pH	Salinity
Irgarol 1051	**0.799**	-0.026	-0.099
M1		**0.718**	0.221
pH			**0.393**

Values in bold denote a significant correlation at 95% ($p<0.05$).

Table 4.

Spearman non-parametric correlation between the concentrations of contaminants and the physicochemical properties of the sediment samples taken from (a) Shoreham Harbour and (b) Brighton Marina, UK.

(a)

	M1	pH	Organic carbon	<63 μm
Irgarol 1051	**0.701**	**-0.620**	**0.619**	**0.440**
M1		**-0.508**	**0.564**	0.294
pH			**-0.608**	**-0.407**
Organic carbon				**0.714**

(b)

	M1	pH	Organic carbon	<63 μm
Irgarol 1051	**0.547**	-0.197	0.221	0.331
M1		**-0.440**	0.286	**0.624**
pH			-0.322	-0.275

Organic carbon	**0.499**

Values in bold denote a significant correlation at 95% ($p<0.05$).

Table 5.

Distribution coefficient and organic carbon normalized partition coefficient for Irgarol 1051 and M1 in Shoreham Harbour and Brighton Marina.

	Shoreham Harbour		Brighton Marina	
	Irgarol 1051	M1	Irgarol 1051	M1
K_d (mL g^{-1})	23-4902	103-5176	18-2886	408-7833
log K_{oc}	3-5	3-5	2-5	1-3